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Chlorination and Evaporation Behaviors of Zinc Oxide in Ar-HCl-O_2 Atmosphere

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Abstract. The chlorination and evaporation behaviors of zinc oxide in an Ar-HCl-O_2 atmosphere were observed by gravimetry. The rate of weight loss increased with increasing partial pressure of hydrogen chloride in an Ar-HCl atmosphere. When the partial pressure of hydrogen chloride in an Ar-HCl atmosphere was the same as that of chlorine in an Ar-Cl_2 atmosphere, the rate of weight loss in the Ar-HCl atmosphere was larger than that in the Ar-Cl_2 atmosphere although the chlorine content in the Ar-HCl atmosphere was half that in the Ar-Cl_2 atmosphere. From the dependence of the rate of weight loss on the partial pressure of hydrogen chloride, it was considered that the rate determining step of the reaction is the diffusion of gaseous species inside the boundary layer in the gas phase. By increasing the partial pressure of oxygen in an Ar-HCl-O_2 atmosphere, the rate of weight loss slightly increased. This tendency was similar to that in an Ar-Cl_2-O_2 atmosphere. On the other hand, the chlorination rate of zinc oxide, estimated by assuming equilibrium of the gas phase, and the measured chlorination rates of Ar-HCl and Ar-Cl_2 gases decreased because of the decrease in partial pressure of hydrogen chloride by the oxidation of HCl gas. It is considered that the increase in the chlorination rate is due to the formation of the oxychloride ZnOCl together with $ZnCl_2$ in the oxidizing atmosphere.

Keywords. Chlorination, dust, recycling, scrap, zinc oxide, hydrogen chloride.

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1 Introduction

Recently, the electric arc furnace (EAF) steelmaking process has become increasingly important from the viewpoint of recycling steel scrap as a steelmaking resource. However, the EAF process generates dust containing many metals such as Fe, Zn, Pb, Cd and so forth [1]. Heavy metal elements contained in the dust would have a harmful effect on the natural environment if the dust was discarded without appropriate treatment, whereas they could be used for the refining of metals if the dust was treated by a suitable recycling process. In Japan, zinc contained in the dust generated from the EAF process is mainly recovered using the Waelz kiln or by the MF process, and recovered zinc oxide is treated by the zinc smelting process [2]. However, the dust from the EAF process also contains a large amount of chlorine derived from waste polyvinyl chloride attached to the scrap, which produces chlorine and hydrogen chloride gases during the high temperature treatment process. Therefore, metal oxides in the dust react with chlorine and hydrogen chloride gases to produce chlorides and oxychlorides. Generally, metal chlorides and oxychlorides have lower melting points and higher vapor pressures than metal oxides. The formation of these chlorides and/or oxychlorides affects the chlorination and evaporation behaviors of metals and also the efficiency of their recovery by treatment processes. Therefore, it is very important to investigate the behaviors of chlorination and evaporation reactions of metal oxides found in dust in a chloridizing atmosphere.

The formation of zinc and lead oxychlorides in an oxidizing atmosphere has been reported in recent studies [3–5]. Therefore, the chlorination reactions of metal oxides during dust treatment are expected to be very complicated. Matsuura et al. measured the chlorination rates of zinc oxide [6], lead oxide [7] and zinc ferrite [8] in various Ar-Cl_2-O_2 atmospheres, and the selective recovery of zinc and lead has also been studied [9]. Chlorination and evaporation reactions can be utilized to recover valuable metals such as zinc and lead from steelmaking dust. The high selective recovery of zinc and lead may be achievable by controlling the partial pressures of chlorine and oxygen within appropriate ranges.

However, considering the practicality of the operation, water contained in the dust and blast air is absorbed by metal chlorides, and hydrated chlorides and/or hydroxides are formed. Therefore, it is expected that a chloridizing atmosphere will contain not only chlorine but also hydrogen chloride. The evaporation behaviors of metals contained in steelmaking dust and municipal solid waste such as K, Na, Si, Fe, Zn and Pb in the gas phase containing water vapor have been reported in various papers [10–15]. However, the

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effect of water vapor on the chlorination and evaporation behaviors of heavy metal elements has not yet been fully clarified because of the formation of oxychlorides in oxidizing and chloridizing atmospheres. In our previous study [16], the effect of water vapor on the evaporation behavior of zinc chloride was investigated at 873 K. The weight loss of zinc chloride decreased with water vapor addition and saturated in an Ar-0.05 atm H_2O atmosphere 20 min after the reaction started. However, the reaction mechanisms between metal oxides and a chloridizing atmosphere containing water vapor are not yet understood. The purpose of the present study is to clarify the mechanisms of the chlorination and evaporation behaviors of zinc oxide in an Ar-HCl-O_2 atmosphere.

2 Experimental

The chlorination and evaporation behaviors of zinc oxide in Ar-HCl and Ar-HCl-O_2 atmospheres were observed by gravimetry. Reagent grade ZnO was used as a specimen. The experimental apparatus was almost the same as that employed in our previous study [16]. The partial pressures of hydrogen chloride and oxygen were controlled by changing the flow rates of Ar, HCl and O_2 gases. The total gas flow rate was varied from 400 to 1000 $\mathrm{cm}^3/\mathrm{min}$. The experimental temperature was controlled from 1023 to 1373 K using a Pt-30%Rh/Pt-6%Rh thermocouple. A sample of 1.0 g ZnO was placed in a mullite boat (width 12 mm, depth 9 mm, length 60 mm) and set in the hot zone of a reaction tube. The experiment started when the experimental gas mixture was introduced into the reaction tube. After each experiment, the weight of the boat with the sample was measured. Some samples were dissolved in nitric acid after chlorination experiments to detect chlorine from the following reaction:

$$\mathrm{Ag}^+\,(\mathrm{aq.}) + \mathrm{Cl}^-\,(\mathrm{aq.}) \rightarrow \mathrm{AgCl}\,(\mathrm{s})\downarrow . \qquad (1)$$

However, no precipitate was found in all solutions. Therefore, no reaction products remained in the residue after experiments, and the reaction residue after the experiment only contained zinc oxide.

3 Results and Discussion

3.1 Chlorination and Evaporation Behaviors of Zinc Oxide in Ar-HCl Atmosphere

Table 1 shows the experimental conditions and the results in an Ar-HCl atmosphere at 1073 K. Figure 1 shows the weight loss with changing time and partial pressure of HCl. Weight loss increased with increasing time and partial pressure of hydrogen chloride. A linear relationship between time and weight loss was observed. Therefore, the rate of weight loss was calculated from the slopes of the straight lines in Figure 1. Figure 2 shows the relationship between the partial pressure of hydrogen chloride and the rate of weight loss of zinc oxide in an Ar-HCl atmosphere compared with that between the partial pressure of chlorine and the rate of weight loss of zinc oxide observed in an Ar-Cl_2 atmosphere [6]. The rate of weight loss in the Ar-HCl atmosphere is larger than that in the Ar-Cl_2 atmosphere at the same partial pressure of hydrogen chloride in the Ar-HCl

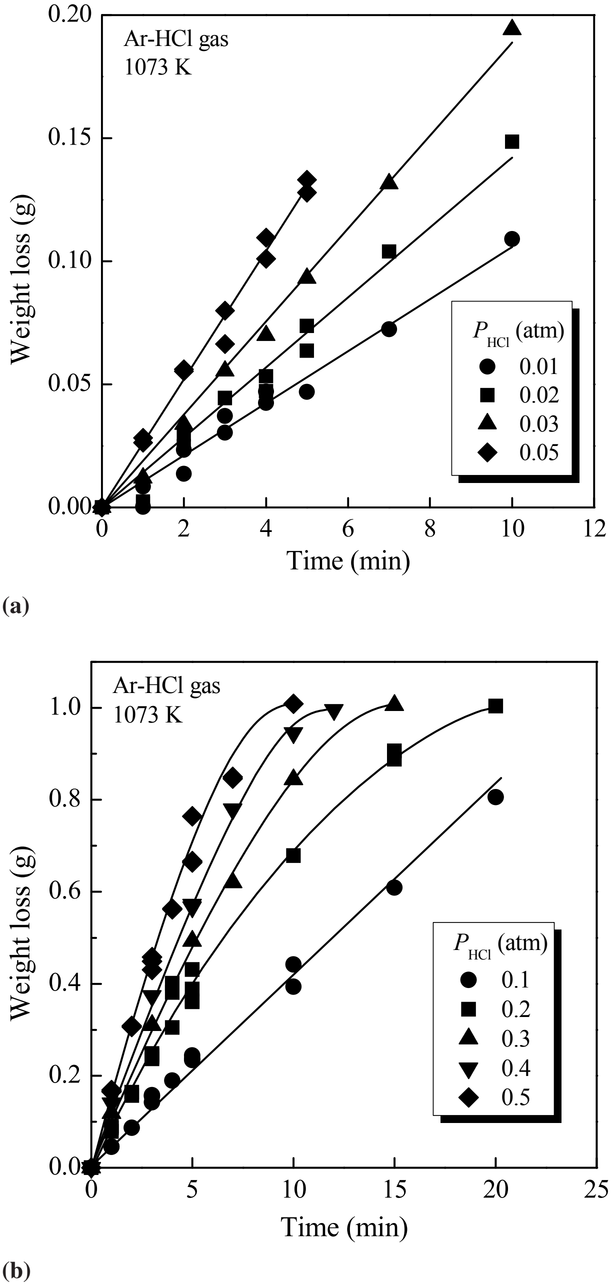


Figure 1. Change in weight loss of zinc oxide with time in Ar-HCl atmosphere at 1073 K, (a) $P_{HCl} = 0.01\text{-}0.05$ atm and (b) $P_{HCl} = 0.1\text{-}0.5$ atm.

Exp. No.	P_{HCl} (atm)	Time (min)	Initial ZnO weight (g)	Weight loss (g)	Rate of weight loss (g/min)
1-001	0.01	1	1.0008	0.0002	0.0106
1-002		1	1.0072	0.0085	
1-003		2	1.0085	0.0137	
1-004		2	1.0051	0.0234	
1-005		3	1.0090	0.0304	
1-006		3	1.0093	0.0371	
1-007		4	1.0028	0.0424	
1-008		4	1.0052	0.0471	
1-009		5	1.0036	0.0469	
1-010		7	1.0110	0.0724	
1-011		10	1.0028	0.1090	
1-012	0.02	1	1.0053	0.0024	0.0142
1-013		1	1.0192	0.0016	
1-014		2	1.0036	0.0248	
1-015		2	1.0186	0.0297	
1-016		3	1.0017	0.0444	
1-017		3	1.0024	0.0445	
1-018		4	1.0178	0.0472	
1-019		4	1.0102	0.0533	
1-020		5	1.0208	0.0737	
1-021		5	1.0035	0.0637	
1-022		7	1.0018	0.1040	
1-023		10	1.0004	0.1485	
1-024	0.03	1	1.0242	0.0120	0.0189
1-025		2	1.0242	0.0337	
1-026		3	1.0111	0.0554	
1-027		4	1.0020	0.0699	
1-028		5	1.0040	0.0931	
1-029		7	1.0236	0.1315	
1-030		10	1.0210	0.1941	
1-031	0.05	1	1.0212	0.0282	0.260
1-032		1	1.0025	0.0263	
1-033		2	1.0219	0.0561	
1-034		2	1.0308	0.0553	
1-035		3	1.0182	0.0799	
1-036		3	1.0016	0.0664	
1-037		4	1.0260	0.1096	
1-038		4	1.0065	0.1010	
1-039		5	1.0279	0.1279	
1-040		5	1.0115	0.1331	
1-041	0.10	1	1.0071	0.0454	0.0417
1-042		1	1.0008	0.0458	
1-043		2	1.0171	0.0871	
1-044		3	1.0213	0.1550	
1-045		3	1.0036	0.1575	
1-046		3	1.0104	0.1420	
1-047		4	1.0300	0.1896	
1-048		5	1.0222	0.2340	
1-049		5	1.0074	0.2438	
1-050		5	1.0294	0.2369	
1-051		10	1.0111	0.4421	
1-052		10	1.0035	0.3938	
1-053		15	1.0024	0.6088	
1-054		20	1.0046	0.8056	

Table 1. Experimental conditions and the results of weight loss of zinc oxide in Ar-HCl atmosphere at 1073 K.

1-055	0.20	1	1.0023	0.0898	0.814
1-056		1	1.0073	0.0790	
1-057		1	1.0112	0.0860	
1-058		2	1.0051	0.1640	
1-059		2	1.0405	0.1571	
1-060		3	1.0045	0.2485	
1-061		3	1.0078	0.2366	
1-062		3	1.0269	0.2408	
1-063		3	1.0401	0.2447	
1-064		4	1.0097	0.4013	
1-065		4	1.0164	0.3047	
1-066		4	1.0312	0.3813	
1-067		5	1.0017	0.4306	
1-068		5	1.0259	0.3604	
1-069		5	1.0364	0.3635	
1-070		5	1.0423	0.3883	
1-071		10	1.0049	0.6783	
1-072		15	1.0017	0.8884	
1-073		15	1.0074	0.9062	
1-074		20	1.0036	1.0036	
1-075	0.30	1	1.0015	0.1184	0.1004
1-076		3	1.0055	0.3100	
1-077		5	1.0013	0.4930	
1-078		7	1.0040	0.6201	
1-079		10	1.0074	0.8443	
1-080		15	1.0056	1.0056	
1-081	0.40	1	1.0034	0.1406	0.1160
1-082		3	1.0067	0.3739	
1-083		5	1.0071	0.5722	
1-084		5	1.0077	0.5666	
1-085		7	1.0015	0.7796	
1-086		10	1.0078	0.9455	
1-087		12	1.0009	0.9955	
1-088	0.50	1	1.0068	0.1690	0.1429
1-089		1	1.0096	0.1660	
1-090		1	1.0030	0.1652	
1-091		2	1.0114	0.3062	
1-092		2	1.0020	0.3088	
1-093		3	1.0020	0.4584	
1-094		3	1.0084	0.4299	
1-095		3	1.0166	0.4491	
1-096		4	1.0092	0.5616	
1-097		4	1.0083	0.5636	
1-098		5	1.0077	0.7644	
1-099		5	1.0115	0.6636	
1-100		5	1.0101	0.6666	
1-101		7	1.0027	0.8459	
1-102		7	1.0018	0.8497	
1-103		10	1.0085	1.0085	

Table 1. contiued

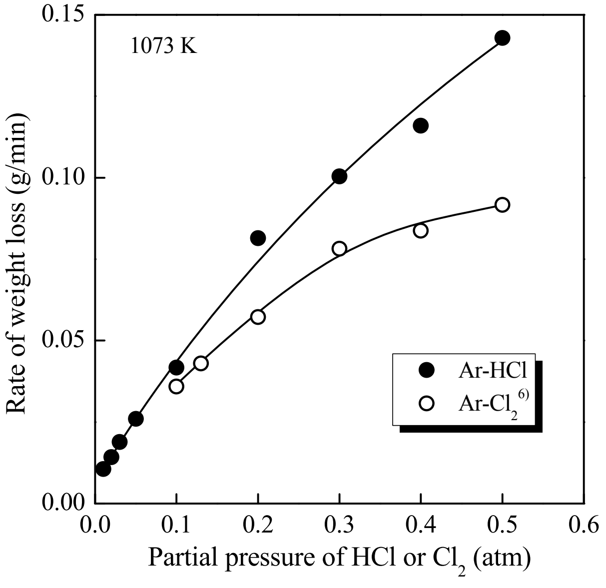


Figure 2. Relationships between the rate of weight loss of zinc oxide and partial pressure of hydrogen chloride in Ar-HCl atmosphere and partial pressure of chlorine in Ar-Cl_2 atmosphere at 1073 K.

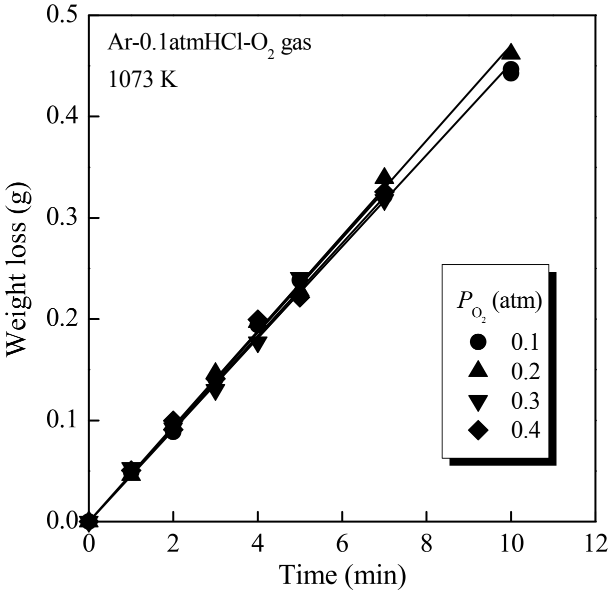


Figure 3. Effect of oxygen partial pressure on the weight loss of zinc oxide with time in Ar-0.1 atm HCl-O_2 atmosphere at 1073 K.

atmosphere and that of chlorine in the Ar-Cl_2 atmosphere, although the number of chlorine atoms in the Ar-HCl atmosphere is half that in the Ar-Cl_2 atmosphere. The relationship between the rate of weight loss and the partial pressure of hydrogen chloride deviated slightly negatively from a linear relationship with increasing partial pressure.

From the dependence of the rate of weight loss on the partial pressure of hydrogen chloride, the rate determining step is considered to be the diffusion of gaseous reactants or products inside the boundary layer in the gas phase. Fruehan and Martonik [17–19] compared the rates of chlorination of several metals and oxides by chlorine and hydrogen chloride. They concluded that the chlorination reaction with hydrogen chloride was controlled by the countercurrent diffusion of hydrogen chloride and the reaction product. In the present experiment, the reaction product, zinc chloride vapor, may have considerable diffusion resistance because of its large molecular weight. The effect of the diffusion resistance of the reaction product on the chlorination rate will increase in an atmosphere with a higher partial pressure of hydrogen chloride because of the larger amount of the reaction product. Therefore, the rate of weight loss deviated negatively from the linear relationship with increasing partial pressure of hydrogen chloride. The effect of the reaction product on the chlorination rate is considered to decrease with increasing gas flow rate, and the rate determining step should change at a higher gas flow rate. However, the effect of the gas flow rate on the reaction rate was measured only at $P_{HCl} = 0.1$ atm in the present study. It is possible that the rate determining step changes with the partial pressure of hydrogen chloride in this study.

3.2 Chlorination and Evaporation Behaviors of Zinc Oxide in Ar-HCl-O_2 Atmosphere

Table 2 shows the experimental conditions and the results in an Ar-HCl-O_2 atmosphere at 1073 K. Figure 3 shows the effect of the partial pressure of oxygen on the weight loss of zinc oxide in an Ar-0.1 atm HCl-O_2 atmosphere. No effect of the oxygen partial pressure was observed. Figure 4 shows the rate of weight loss obtained from the slopes of the lines shown in Figure 3 with changing partial pressure of oxygen in an Ar-0.1 atm HCl-O_2 atmosphere compared with that in an Ar-0.1 atm Cl_2-O_2 atmosphere [6]. Upon adding oxygen to the Ar-HCl atmosphere, the rate of weight loss slightly increased; this tendency is the same as that observed in an Ar-Cl_2-O_2 atmosphere.

It is considered that the rate of weight loss changes when hydrogen chloride is oxidized to form chlorine gas and water vapor according to reaction (2):

$$2\mathrm{HCl}\,(g) + \frac{1}{2}\mathrm{O_2}\,(g) = \mathrm{Cl_2}\,(g) + \mathrm{H_2O}\,(g)\,. \quad (2)$$

Since the rate of weight loss in the Ar-HCl atmosphere was larger than that in the Ar-Cl_2 atmosphere when the partial pressure of hydrogen chloride in Ar-HCl gas was the same as that of chlorine in Ar-Cl_2 gas at 1073 K, the oxidation of hydrogen chloride should cause this decrease in the rate of weight loss. The partial pressures of hydrogen chloride, chlorine, oxygen and water vapor in equilibrium were

Exp. No.	P_{O2} (atm)	Time (min)	Initial ZnO weight (g)	Weight loss (g)	Rate of weight loss (g/min)
2-001	0.10	1	1.0013	0.0487	0.0453
2-002		2	1.0123	0.0885	
2-003		3	1.0173	0.1408	
2-004		4	1.0112	0.1942	
2-005		5	1.0242	0.2383	
2-006		7	1.0024	0.3215	
2-007		10	1.0174	0.4426	
2-008		10	1.0067	0.4466	
2-009	0.20	1	1.0109	0.0456	0.0471
2-010		2	1.0253	0.0956	
2-011		3	1.0052	0.1464	
2-012		4	1.0019	0.1969	
2-013		5	1.0214	0.2279	
2-014		7	1.0226	0.3392	
2-015		10	1.0289	0.4620	
2-016	0.30	1	1.0046	0.0530	0.0458
2-017		2	1.0256	0.0924	
2-018		3	1.0089	0.1301	
2-019		4	1.0191	0.1771	
2-020		5	1.0109	0.2410	
2-021		7	1.0020	0.3178	
2-022	0.40	1	1.0134	0.0505	0.0467
2-023		2	1.0064	0.0908	
2-024		2	1.0256	0.0995	
2-025		3	1.0267	0.1411	
2-026		4	1.0253	0.1995	
2-027		5	1.0046	0.2216	
2-028		7	1.0228	0.3255	

Table 2. Experimental conditions and the results of weight loss of zinc oxide in Ar-0.1 atm HCl-O_2 atmosphere at 1073 K.

calculated using FactSage 6.0 software from the initial gas composition and temperature. The rates of weight loss corresponding to hydrogen chloride and chlorine gases were estimated from the relationships shown in Figure 2 and the calculated equilibrium partial pressures of hydrogen chloride and chlorine.

Figure 5 shows the estimated rate of weight loss in an Ar-0.1 atm HCl-O_2 atmosphere compared with the observed result. The rate of weight loss due to chlorination by hydrogen chloride decreases with increasing oxygen partial pressure as explained above, while that due to chlorination by chlorine increases owing to the formation of chlorine gas according to reaction (2). As a result, the total rate of weight loss decreases with increasing oxygen partial pressure if gas phase equilibrium is attained. Therefore, it is concluded that the addition of oxygen increases the rate of weight loss of ZnO, regardless of the achievement of gas phase equilibrium. Since the relationship shown in Figure 2 does not include the effect of oxygen gas on the chlorination of ZnO, the difference between the measured and estimated rates is attributed to the effect of oxygen gas. The formation of zinc oxychloride species such as ZnOCl [3,5] together with $ZnCl_2$ is enhanced in the oxidizing atmosphere, and thus the rate of weight loss will increase with the addition of oxygen in a chloridizing atmosphere.

3.3 Effect of Temperature

Table 3 shows the experimental conditions and the results in an Ar-0.1 atm HCl atmosphere at various temperatures. The overall rate constant was calculated from the measured rate of weight loss assuming a surface area of about 3.9 cm^2 (7 mm × 56 mm). Figure 6 shows the relationship between the overall rate constant of weight loss in an Ar-0.1 atm HCl atmosphere and the gas flow rate at 1023 to 1373 K. Since the overall rate constant increased with increasing gas flow rate between 400 and 1000 cm^3/min, it is considered that the chlorination reaction was controlled by the gas phase mass transfer under the measured conditions. In addition, on obvious effect of temperature on the rate constant of weight loss was observed. Small activation energies for the chlorination reaction of Cu by Cl_2 have been reported

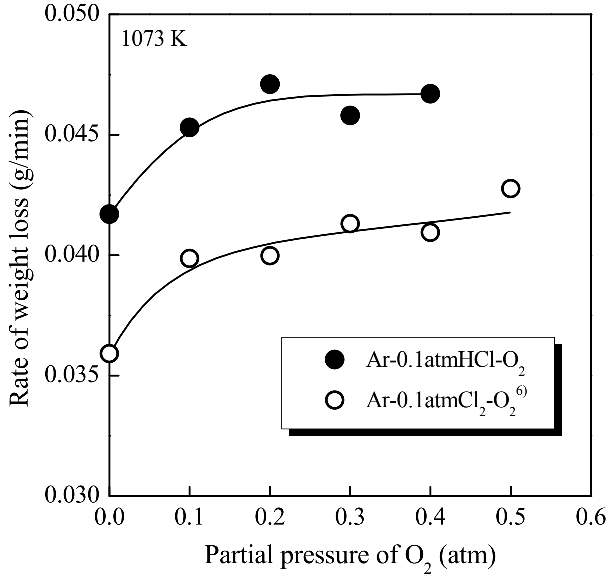


Figure 4. Effect of oxygen partial pressure on the rate of weight loss of zinc oxide in Ar-0.1 atm HCl-O$_2$ atmosphere and Ar-0.1 atm Cl$_2$-O$_2$ atmosphere at 1073 K.

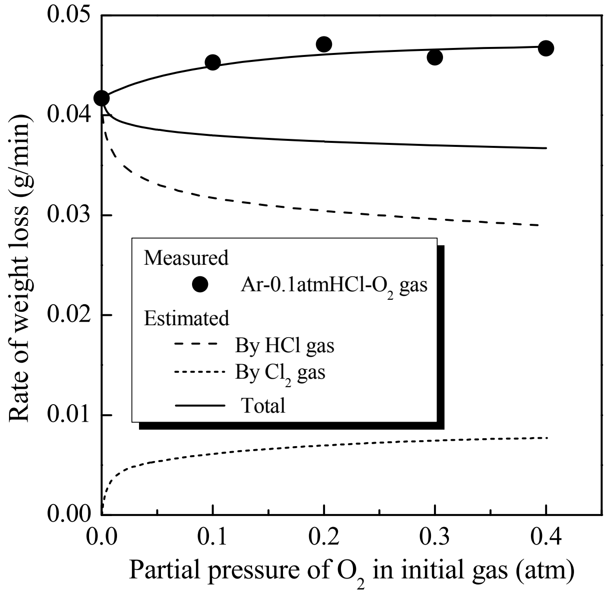
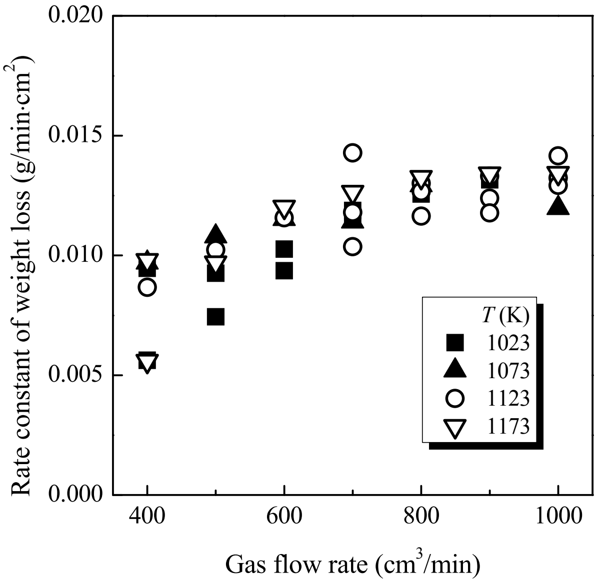
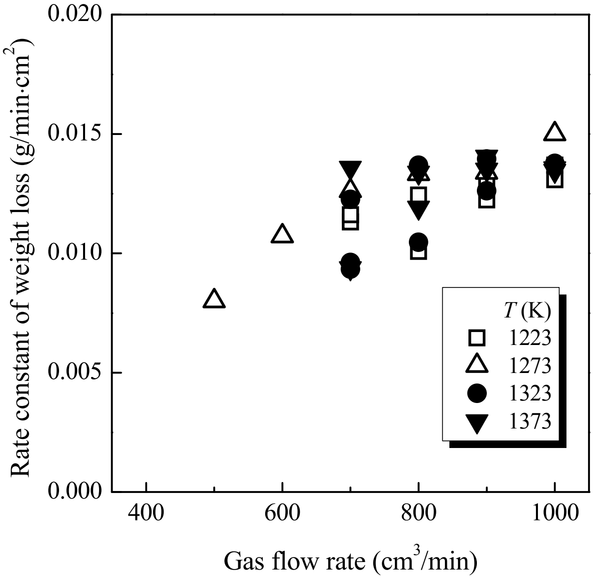


Figure 5. Estimated rate of weight loss in Ar-0.1 atm HCl-O$_2$ atmosphere compared with measured rate at 1073 K.

by Frommer and Polanyi [20], and for that of Ni by Cl$_2$ by McKinley and Shuler [21]; in both reactions the activation energy was no more than 8 kJ/mol. As discussed by Fruehan and Martonik [17–19], it is considered that the rate determining step is the diffusion of gaseous species inside the boundary layer in the gas phase because of the large molecular weight of chloride vapor.



(a)



(b)

Figure 6. Relationship between rate constant of weight loss and the gas flow rate in Ar-0.1 atm HCl atmosphere in the temperature range of (a) 1023 and 1173 K, and (b) 1223 and 1373 K.

4 Conclusions

The chlorination and evaporation behaviors of zinc oxide in an Ar-HCl-O$_2$ atmosphere were measured. The results are summarized as follows.

(1) The rate of weight loss of zinc oxide increased with increasing partial pressure of hydrogen chloride. The rate

Exp. No.	Temp (K)	Gas flow rate (cm^3/min)	Initial ZnO weight (g)	Weight loss (g)	Rate of weight loss (g/min)
3-001	1023	400	1.0150	0.0438	0.0219
3-002		400	1.0401	0.0739	0.0369
3-003		500	1.0189	0.0579	0.0290
3-004		500	1.0120	0.0722	0.0361
3-005		600	1.0586	0.0731	0.0365
3-006		600	1.0016	0.0800	0.0400
3-007		700	1.0131	0.0898	0.0449
3-008		700	1.0152	0.0926	0.0463
3-009		800	1.0153	0.0979	0.0490
3-010		900	1.0205	0.1025	0.0513
3-011		1000	1.0392	0.1027	0.0513
3-012	1073	400	1.0414	0.0756	0.0378
3-013		500	1.0299	0.0841	0.0421
3-014		600	1.0321	0.0898	0.0449
3-015		700	1.0168	0.0891	0.0445
3-016		800	1.0108	0.1009	0.0504
3-017		1000	1.0211	0.0935	0.0467
3-018	1123	400	1.0328	0.0676	0.0338
3-019		500	1.0025	0.0797	0.0399
3-020		600	1.0238	0.0902	0.0451
3-021		700	1.0049	0.1114	0.0557
3-022		700	1.0082	0.0808	0.0404
3-023		700	1.0079	0.0920	0.0460
3-024		800	1.0227	0.1013	0.0507
3-025		800	1.0084	0.0909	0.0454
3-026		800	1.0098	0.0988	0.0494
3-027		900	1.0246	0.1037	0.0519
3-028		900	1.0063	0.0966	0.0483
3-029		900	1.0135	0.0917	0.0459
3-030		1000	1.0324	0.1103	0.0552
3-031		1000	1.0230	0.1031	0.0516
3-032		1000	1.0244	0.1009	0.0504
3-033	1173	400	1.0322	0.0436	0.0218
3-034		400	1.0192	0.0765	0.0382
3-035		500	1.0304	0.0755	0.0378
3-036		600	1.1225	0.0937	0.0469
3-037		700	1.0248	0.0986	0.0493
3-038		800	1.0252	0.1034	0.0517
3-039		900	1.0181	0.1047	0.0523
3-040		1000	1.0169	0.1049	0.0524
3-041	1223	700	1.0037	0.0882	0.0441
3-042		700	1.0170	0.0906	0.0453
3-043		800	1.0263	0.0785	0.0393
3-044		800	1.0232	0.0970	0.0485
3-045		900	1.0240	0.0955	0.0477
3-046		900	1.1074	0.1006	0.0503
3-047		1000	1.0260	0.1019	0.0510
3-048		1000	1.0024	0.1068	0.0534

Table 3. Experimental conditions and the results of weight loss of zinc oxide in Ar-0.1 atm HCl atmosphere at various temperatures for a reaction time of 2 min.

3-049	1273	500	1.0134	0.0623	0.0312
3-050		600	1.0237	0.0837	0.0418
3-051		700	1.0380	0.0985	0.0492
3-052		800	1.0069	0.1041	0.0520
3-053		900	1.0330	0.1045	0.0522
3-054		1000	1.0221	0.1169	0.0585
3-055	1323	700	1.0075	0.0750	0.0375
3-056		700	1.0161	0.0728	0.0364
3-057		700	1.0299	0.0957	0.0478
3-058		800	1.0061	0.1067	0.0534
3-059		800	1.0066	0.0816	0.0408
3-060		900	1.0033	0.0983	0.0492
3-061		900	1.0221	0.1087	0.0544
3-062		1000	1.0134	0.1074	0.0537
3-063		1000	1.0142	0.1071	0.0535
3-064	1373	700	1.0289	0.0732	0.0366
3-065		700	1.0069	0.1061	0.0530
3-066		800	1.0125	0.0929	0.0465
3-067		800	1.0015	0.1044	0.0522
3-068		900	1.0093	0.1054	0.0527
3-069		900	1.0192	0.1095	0.0548
3-070		1000	1.0114	0.1049	0.0525
3-071		1000	1.0029	0.1057	0.0529

Table 3. continued

determining step is considered to be the diffusion of gaseous reactants or products in the gas phase.

(2) The addition of oxygen in an Ar-HCl atmosphere slightly increased the rate of weight loss of zinc oxide. This is due to the formation of zinc oxychlorides such as ZnOCl together with $ZnCl_2$.

(3) The overall rate constant of the chlorination reaction for zinc oxide in an Ar-0.1 atm HCl atmosphere increased with increasing gas flow rate between 400 and 1000 cm^3/min at 1023 to 1373 K. It is considered that the chlorination reaction was controlled by the gas phase mass transfer under the measured conditions. No obvious effect of temperature on the rate constant of the chlorination reaction of zinc oxide by hydrogen chloride was observed.

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